The Hydration Products of a Refractory Calcium Aluminate Cement at Low Temperatures

Nilforoushan, Mohammad Reza*+; Talebiaan, Nasrien
Islamic Azad University, Shahreza Barnch, P.O. Box 86145-311 Shahreza, I.R. IRAN

ABSTRACT: *Calcium aluminates (CA) are the most important hydraulically setting cements used for preparing refractory castables, because they develop high strength at very early ages after placements. The anhydrous phases of this kind of cements are CA, CA_2 and traces of $C_{12}A_7$ and alpha-alumina. The major hydraulic phase in all of the CA cements including ciment fondue is CA. Once hydrated, it starts to form the hexagonal crystals of CAH_{10} and C_2AH_8 that depending on the time and temperature of hydration converts to the cubic crystals of C_3AH_6 and AH_3. The nature of the calcium aluminate hydrates, their morphology and the way in which they are broken down, play an important roles in determining the properties of fired cement. For this reason a series of investigations has been conducted on the hydration reactions of Secar 71, a commercial cement which can completely represents this type of cements, and hydration products were characterized by DTA, DSC, XRD and SEM. At 12 °C, the only hydration products were a gel phase, CAH_{10} and gibbsite, while the same hydrates were still predominant phases, C_4ACH_{11} also formed as a result of carbonation of the pastes.*

KEY WORDS: *Calcium aluminate cement (CAC), Hydration reactions, CAH_{10}, C_2AH_8, C_3AH_6, AH_3.*

INTRODUCTION

Calcium aluminate cements are a group of interrelated cementious materials, with alumina contents varying from about 38 % to 90 %, which incorporate calcium mono aluminate ($CaAl_2O_4$ or CA) as the major constituent. Second phases are always present, but vary with the lime:alumina ratio and with the level of impurities, especially silicon and iron. The most refractory cement, ie. >70 % Al_2O_3, are usaually low in iron and silicon and are, therefore, white in color and almost pure members of the $CaO-Al_2O_3$ binary system [1-3]. In all the calcium aluminate cements CA is the major component.

CA reacts with water to form a series of calcium aluminate hydrates, which vary with temperature and time. At low temperatures (<18 °C) the only crystalline hydrate formed is CAH_{10} ($CaO.Al_2O_3.10H_2O$), the microstructure of this phase in hydrated cement is not fully understood although, an amorphous phase is formed in considerable amounts. At higher temperatures and in cements containing $C_{12}A_7(12CaO.7Al_2O_3)$, C_2AH_8 ($2CaO.Al_2O_3.8H_2O$) is formed as well as or instead of CAH_{10} [4-5]. Both of these hydrates are hexagonal in morphology and thermodynamically metastable.

Table 1: Chemical composition of Secar 71.

Oxide	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	SiO_2	Na_2O	K_2O	SO_3	LOI
W %	70-72	26-29	<0.05	<0.3	<0.1	<0.8	<0.3	<0.3	<0.3	----

Above 28 ℃ they convert relatively rapidly into C_3AH_6 ($3CaO.Al_2O_3.6H_2O$), which has a cubic structure and gibbsite AH_3 ($Al_2O_3.3H_2O$) or $Al(OH)_3$. The conversion products are denser than hexagonal hydrates. Although the presence of major hydrates, CAH_{10}, C_2AH_8 and AH_3, can be detected by X-ray diffraction (XRD), the peaks are not readily suitable for quantitative determination. Also there are certain phases, which are amorphous by nature, e.g. the gel phases and the presence of these will not be detected by XRD. Therefore, the use of thermal analysis techniques is very important in the study of cements as it gives information as to the hydrate phases present in the early stages of hydration, when this may not be possible from XRD. However, comparison of the thermal analysis curve with complementary data from additional techniques allows a clearer, more accurate interpretation of the trace to be made as some anomalies do occur.

Some workers have investigated synthetic routes for preparation of calcium aluminate cement powder as well as its pure anhydrous phases. Most of them tried it through solid state sintering while others tried chemical routes but in almost all cases people tried to investigate the hydration properties of the prepared products by XRD, FTIR, SEM, DTA, DSC and EDXS [6-9].

As various people have talk about the conversion reactions and the deterioration it can cause in structural concretes when it is made by high alumina cements, there has not been any clear understanding from the morphology of hydrates, the extend of time, and temperature that conversion takes place, and the microstructure of the converted concretes. Since it has very important impact on the application properties of calcium aluminate cements, in this study attempts has been taken to investigate the hydration reactions of a refractory calcium aluminate cement at low temperatures such as 12 and 20 ℃ in order to have a clear understanding from the nature, morphology and the extend in which conversion of different phases may take place, and characterize the hydration products by various techniques such as Differential scanning calorimeter

Table 2: Examples of mineralogical compositions of calcium Aluminate Cements.

Unhydrous phase	Secar 71
CA	***
CA2	***
C12A7	*
A	*
C2S	-
C2AS	-
C4AF	-

(DSC), Differential thermal analysis (DTA), X-ray diffraction (XRD) and Scanning electron microscopy (SEM).

EXPERIMENTAL

Hydration studies were carried out using Secar 71, the product of Lafarge Company in France. The chemical and mineralogical compositions based on the data extracted from information given by company are listed in tables 1 and 2 respectively.

Pastes and slurries were prepared by mixing cement powder with boiled distilled water, which had been equilibrated at the appropriate temperature. Mixing was carried out by hand, the paste poured into moulds, put into plastic bag and then into a water bath maintained at a controlled temperature. To prepare samples for various instruments, the ground powder was passed through the appropriate sieve. Freshly fractured samples were used for SEM investigations. The pastes were mounted on stubs using electrode silver paint and coated with carbon or gold. The prepared samples were examined on a Cambridge cam scan microscope, operating at 20 KV and a spot size of 320 °A. The differential scanning calorimeter was a Dupont 2000 instrument. This was linked to a PC computer. A heating rate of 10 ℃/min was used from 25 ℃ to 500 ℃. All samples were run in an atmosphere of dry nitrogen flowing at 120 ml/min. A Stanton-Redcroft 67-3 DTA was used in this study

Table 3: X - ray peak height measurements of Secar 71 hydrated at 12 ºC.

n	Hydration time	CA (cm)	CA$_2$ (cm)	CAH$_{10}$ (cm)	C$_2$AH$_8$ (cm)	C$_3$AH$_6$ (cm)	AH$_3$ (cm)
1	--	27.4	18.5	---	--	--	--
2	2 hrs	26.5	17.2	2.4	ND	ND	ND
3	4 hrs	26.3	16.4	2.8	ND	ND	ND
4	6 hrs	12.8	16.2	7.0	ND	ND	2.4
5	1 day	12.6	15.9	11.0	ND	ND	3.2
6	3 days	12.2	13.8	13.0	ND	ND	4.2
7	5 days	11.8	13.8	14.6	ND	ND	4.6
8	7 days	10.7	13.8	15.6	ND	ND	5.2

with platinum crucibles in which a sample weight (ground powder) of 100 mg was used in each run. Alumina reference of the same weight was also used. Analysis was carried out in argon flow of 15 ml/min at a heating rate of 10 ºC /min.

RESULTS AND DISCUSSION

The hydration product of calcium aluminate cement varies with time and temperature. Two different temperatures at various times were used based on the nature of hydration product forms at these temperatures, which were 12 and 20 °C.

Hydration reactions at 12 °C

As was mentioned in the experimental part, cement was left in the water bath after mixing with water, sample of the pastes removed at certain time intervals and quenched with acetone to stop further hydration. Samples of the powder hydrated at 12 °C were examined by X-ray diffraction. Results of peak height measurements, as representative for the amounts of the phase, made on the most intense peaks attributed to certain phases are summarized in table 3.

It can be seen from the table that the intensity of the peaks of CA and CA$_2$ decreased as the time of hydration increased. The major hydration product formed at this temperature was CAH$_{10}$, the most intense peak of it is at 2-theta 11.2, the intensity of the X-ray peaks corresponding to the formation of this phase increased with increasing the time of hydration. Traces of gibbsite were also detected by X-ray diffraction after 6 hours of

hydration and increased after longer time of hydration. Two other major peaks shown in the pattern are attributed to the unhydrous phases present in cement that is CA and CA$_2$, the most intense peak of former is at 2-theta 30.2 and the latter at 25.4, the intensity of the peaks decreased by extending the hydration time. No other hydration products such as C$_2$AH$_8$ and C$_3$AH$_6$ were detected by X-ray diffraction at this temperature. Traces of the X-ray diffraction patterns taken from the paste are also shown in Fig. 1.

Some other portions of the sample were examined by differential scanning calorimetery and the resulting endothermic peaks are shown in Fig. 2. According to the figure, the paste hydrated for two hours shows only a hint of a very broad peak around 130 ºC, which is possibly attributed to the formation of the gel phase or CAH$_{10}$. By increasing the time of hydration to 4 and 6 hours, a trace of gibbsite was also formed which is shown by a weak peak at around 280 ºC. Increasing the time of hydration to one day, a large endothermic peak at around 115 ºC can be attributed to the gel phase, followed by a weaker endothermic peak at around 150 ºC due to the formation of some CAH$_{10}$. The peaks at 270 and 290 ºC may both be attributed to the formation of gibbsite, since no sign of formation of C$_3$AH$_6$ was detected by X-ray diffraction. The DSC curves do not change in their essential features As the time of hydration increased up to 7 days, although the magnitude of the AH$_3$ peak continued to increase. The major peak in all curves from 1 day to 7 days was that attributed to the gel phase.
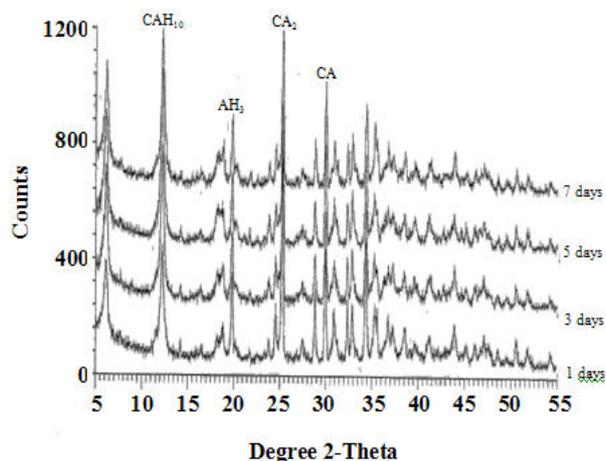
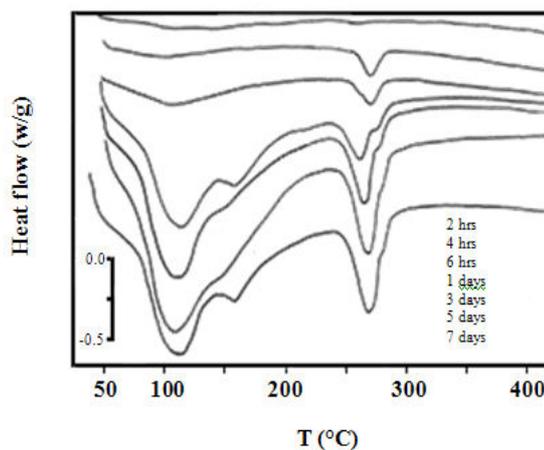***Fig. 1: X-ray peak height of Secar 71 hydrated at 12 ºC.***

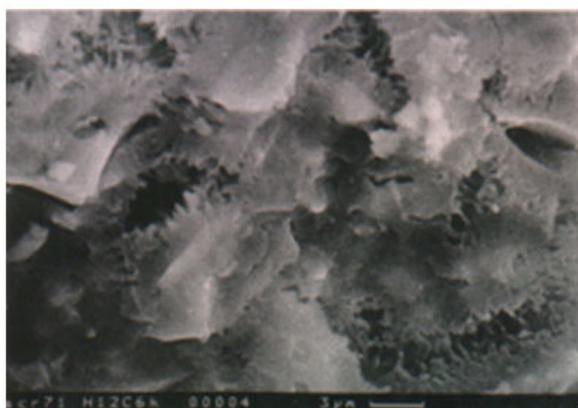***Fig. 2: DSC thermographs of the Secar 71 hydrated at 12 ºC.***

Fig. 3: SEM micrograph of Secar71 hydrated for 1 day at 12 ºC (------ 10μm).

Fig. 4: SEM micrograph of Secar 71 hydrated for 10 months at 12 ºC (------ 3 μm).

The results of the X-ray and DSC patterns are very well correlated, although XRD cannot detect the gel phase. In order to investigate the actual morphology of the crystals formed at 12 ºC, parts of the fractured surface of the paste was also examined by scanning electron microscope. Two of the electron micrographs best showed the morphology of crystals and are brought here in Figs. 3 and 4.

The former is from the pastes hydrated for one day and the latter is other part of the same paste hydrated after 10 months. CAH_{10} has tiny hexagonal prisms shapes at the early stages of hydration which is shown in Fig. 3 while, when hydration continues for longer times the morphology of these crystals slightly changes, crystals grows and takes the morphology similar to one shown in Fig. 4.

Hydration at 20 °C

Hydration behavior of the pastes made from Secar 71 was also investigated at 20 ºC. It seemed from the results that predominant hydration product is still CAH_{10} and $C_4A\bar{C}H_{11}$ which forms as a result of carbonation that might be, due to the pre-carbonation of mixing water at this temperature.

The results of X-ray diffraction pattern investigated on the powder of the paste showed that the first hydrate formed after 4 hours of hydration was AH_3 accompanied by traces of $C_4A\bar{C}H_{11}$. Both phases were formed in increasing quantities as hydration progressed. Traces of CAH_{10} and C_3AH_6 also started to form after 4 days of hydration. Comparison of the peak height measurements made on the X-ray diffraction patterns of the pastes hydrated at various time are summarized graphically in Fig. 5.
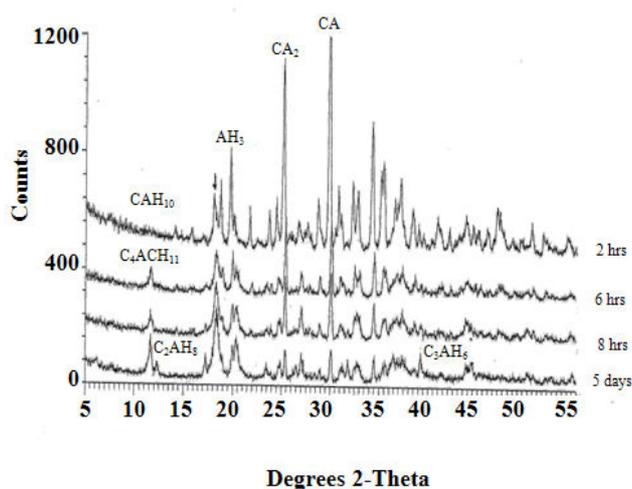
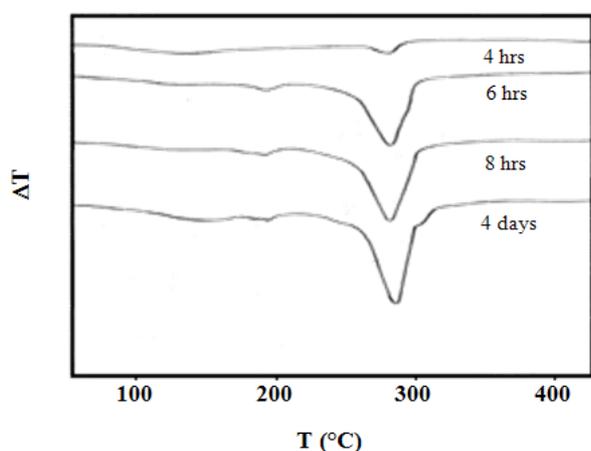***Fig.5: X-ray diffraction patterns of the phases formed at 20 ℃.***

Fig. 6: DTA thermographs of the paste hydrated at 20 ℃.
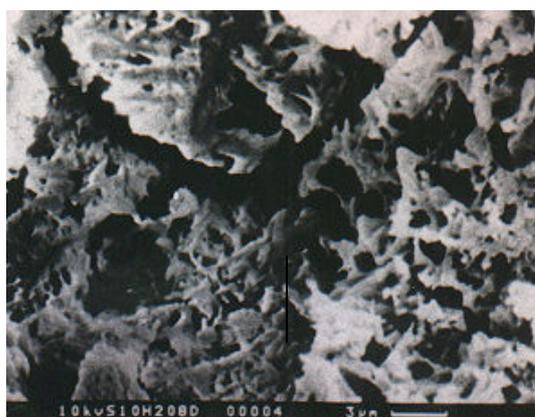

Fig. 7: SEM micrograph of Secar 71 hydrated for 8 day at 20 ℃ (------ 3 μm).

Investigations were made on the other parts of the pastes hydrated from 4 hours up to 4 days by differential thermal analysis. The thermographs taken from the pastes at various times are summarized in Fig. 6. It seems that the starting hydrate that forms after 2 hours of hydration is AH_3 the peak that appears due to decomposition of this phase is at 290 ℃, followed by another shoulder at around 195 ℃ attributed to $C_4A\bar{C}H_{11}$. Another peak, which is like a shoulder at 310 ℃ on the peak of the paste hydrated for 4 days is attributed to the formation of C_3AH_6, this has also been confirmed by X-ray diffraction too. Formation of CAH_{10} started after 4 hours; a broad peak at 120 ℃ shows this.

Electron micrographs taken from fractured surface of the pastes hydrated at 20 ℃ after 8 days of hydration shows that CAH_{10} and $C_4A\bar{C}H_{11}$ has almost the same morphology which are not distinguishable from each other. This electron micrograp is shown in Fig. 7.

CONCLUSIONS

1 - Based on the experimental results of this study, the nature of the hydration products formed from Secar 71 varies with the temperature of hydration.

2 - At 12 ℃ the only three-hydration products of Secar 71 are an amorphous gel phase, CAH_{10} and AH_3 and no conversion to C_3AH_6 took place. Investigations made by SEM on the paste hydrated at this temperature revealed that CAH_{10} has tiny hexagonal prism shapes at the beginning of hydration but the morphology of it changes when hydration reactions continue for longer times.

3 - At 20 ℃ CAH_{10} and AH_3 are still the predominant phases, but $C_4A\bar{C}H_{11}$ also formed which is possibly due to the carbonation of the pastes prior to the time when hydration reaction starts. Electron micrographs taken from fractured surface of the pastes showed that, CAH_{10} and $C_4A\bar{C}H_{11}$ have almost the same morphology which were not distinguishable from each other.

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